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J.M. Deutsch. The dynamics of entangled polymers. Journal de Physique, 1987, 48 (1), pp.141-150.
10.1051/jphys:01987004801014100 . jpa-00210416

HAL Id: jpa-00210416

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Classification
Physics Abstracts
46.60 — 61.25

The dynamics of entangled polymers

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(Reçu le 20 mars 1986, révisé le 4 août, accepté le 21 août 1986)

Résumé. — On étudie la dynamique des chaînes polymériques linéaires en solutions concentrées. Ce travail est basé sur le modèle de « reptation » de de Gennes qui constitue une théorie du mouvement d'un polymère en présence de nombreuses contraintes topologiques. On présente ici un travail théorique et numérique qui étend cette théorie aux interactions à plusieurs chaînes. On présente un argument théorique qui donne le comportement d'échelle du plus long des temps de relaxation d'une fondu de polymères en fonction du poids moléculaire M des chaînes individuelles. Le résultat principal est que ces interactions de volume exclues modifient le temps de relaxation de M^3 à $M^3 \exp(\text{const. } M^{2/3} + O(M^{1/3}))$. Cette nouvelle théorie est, dans une large mesure, en accord avec une simulation directe du modèle de reptation qui incorpore de nombreuses interactions de volume exclues des chaînes.

Abstract. — The dynamics of linear chain polymers is studied in concentrated solutions. This paper is based on the « reptation » model of de Gennes, which is a theory of the motion of a polymer in the presence of many topological constraints. Here theoretical and numerical work is presented to extend this theory to include many chain interactions. A theoretical argument is presented that gives the scaling behaviour of the longest relaxation time of a polymer melt as a function of the molecular weight M of individual chains. The main prediction is that these excluded volume interactions alter the relaxation time from M^3 to $M^3 \exp(\text{const.} \times M^{2/3} + O(M^{1/3}))$. This new theory agrees in many respects with a direct simulation of the reptation model that incorporates many chain excluded volume interactions.

1. Introduction.

The viscoelastic properties of linear chain polymer melts and concentrated solutions have been studied extensively [1] as a function of molecular weight of individual chains. When the number of monomeric units on a chain exceeds a critical value, which corresponds to a molecular weight of M_c , the system starts to exhibit an elastic response to external stress over some duration of time. We denote this time the relaxation time t_{rel} . For time scales longer than t_{rel} the polymers behave like a liquid. Above M_c , the viscosity appears to obey the empirical relation

$$\eta \propto M^{3.4}. \quad (1)$$

The purpose of this paper is to propose a theory and present numerical evidence which explains this empirical observation. Over all, experimental data on concentrated polymers are reasonably well explained by the reptation model [2, 3]. In the next section, reptation is reviewed, and I will only mention now that the reptation model predicts

$$\eta \propto M^3 \quad (2)$$

which is a significant deviation from experimental results, but presumably not enough to warrant abandoning reptation as an approach. The main result of this work is that incorporating another physical effect, many chain interactions, that was left out of the simple reptation model leads to predictions that agree better with experiment, namely equation (1). In order to study what the effects of these interactions are, I have done both theoretical and numerical work. I present the numerical work first, in section 3, and the theoretical investigation in section 4. In section 5, I give some tentative ideas concerning corrections to the reptation model, and in section 6, I conclude by comparing my work with experimental data.

2. The reptation model.

In this model, to calculate the motion of one polymer, we assume that the net effect of the other polymers is to confine the polymer of interest to a « tube ». In other words the polymer cannot move perpendicular to the direction of the tube by more than a tube diameter, as illustrated in figure 1. The only modes of motion allowed are ones that allow

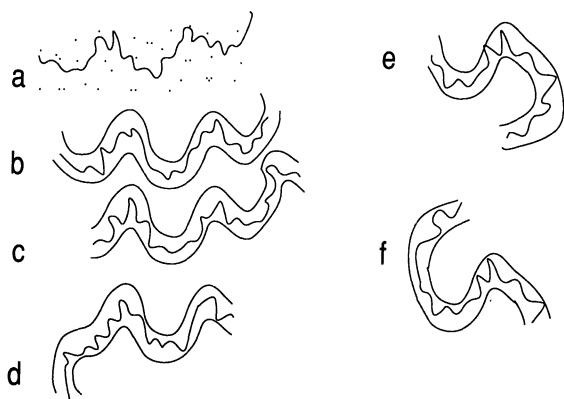


Fig. 1. — A polymer chain reptating. (a) The idealized motion of a polymer chain through other polymer chains. The solid curve represents a section of polymer, the other polymers are represented by dots. (b) A picture of the tube with the polymer wriggling inside it. For short times, the motion of a monomer is that of local relaxation along the tube. (c), (d), (e) and (f) The tube changing position owing to the motion of the chain as a whole.

diffusion along the direction of the tube. As the polymer moves, it will form new pieces of tube and destroy old pieces of tube at the two ends of the polymer. Eventually it will loose all correlation with its initial tube, as the polymer will have formed a completely new tube. The time it takes to do this (the reptation time t_{rep}) scales as M^3 . This is because the friction coefficient ν , along the direction of the tube is proportional to M , so that the time it takes a point in the middle of the chain to diffuse out to the end of the initial tube is proportional to $\nu M^2 = M^3$, which should scale as t_{rep} . Other predictions of the reptation model are that the elastic modulus $G(t)$ has a plateau up to a time of order the reptation time, and that the value of $G(t)$ at this plateau is independent of M . This is because for times much less than the reptation time, entanglements act as crosslinks as in rubber, and the number of crosslinks is independent of chain length. The plateau in $G(t)$ and the independence of its magnitude as a function of M are indeed observed experimentally [4] which is further evidence for the experimental validity of the reptation model. However the viscosity is related to $G(t)$ by

$$\eta = \int_0^\infty G(t) dt. \quad (3)$$

So since the value of the plateau of $G(t)$ is independent of M , the relaxation time t_{rel} should scale as the viscosity does namely $t_{\text{rel}} \propto M^{3.4}$. This differs from the reptation model which has $t_{\text{rel}} \propto t_{\text{rep}} \propto M^3$.

3. Numerical work.

Consider N chains on a lattice of dimensions $B \times B \times B$. Each chain is M steps long and no two

monomers can occupy the same lattice site. The dynamics that I employ are called « reptation dynamics » [5]. In the case of no excluded volume this is equivalent to the « primitive chain model » of Doi and Edwards [3]. We clip of the end monomer of a chain at random. Then an attempt is made to add it to the other end of the clipped polymer in some randomly chosen direction. If the lattice site we are trying to place the monomer on is already occupied, we reject the move. Otherwise it is accepted, and the whole process begins again. This procedure is illustrated in figure 2. Note that in this model, the time step Δt is not really independent of molecular weight, but should be proportional to M . As mentioned above, if we take out the excluded volume constraint this model gives $t_{\text{rep}} = \Delta t M^2 = M^3$. However we will see that the situation is substantially changed when we put in the excluded volume constraint. « Skew » boundary conditions were used for most of this work, with some simulations being run with periodic boundary conditions. No detectable difference between these two boundary conditions was encountered.

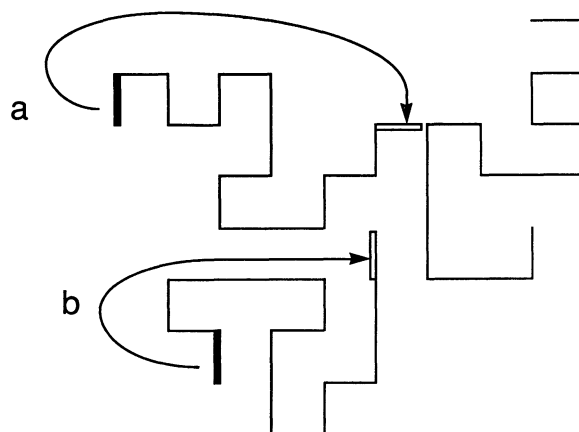


Fig. 2. — An illustration of reptation dynamics. In (a), one end (painted black) attempts to move to a new position (shown in white). This attempt is rejected since the new site is already occupied. On the other hand, the move shown in (b) succeeds since the white monomer has filled a vacant site.

To equilibrate the systems, an initial system was moved until almost all the polymers had escaped from their original tubes, and this process was repeated at least several times. Statistical properties were checked and showed that after this equilibration process, static correlations were in thermal equilibrium. These equilibrated systems, were then run and dynamical correlations were measured as described below. Averaging was performed until satisfactory convergence was achieved, ranging from 6 to over 100 statistically independent runs.

Using the above model, I have computed a variety of dynamical correlation functions for different systems. I have discussed a more limited numerical

analysis done at only one chain length, but which also looked at the case of no excluded volume, previously [6]. I will now define the correlation functions used in my simulations.

The monomer-monomer displacement $\langle r^2(t) \rangle$ is given by

$$\langle r^2(t) \rangle = \frac{1}{L} \left\langle \sum_{i=1}^L [r_i(t) - r_i(0)]^2 \right\rangle \quad (4)$$

where $r_i(t)$ is the position of the i th bead of a chain at time t . The average denoted by angled brackets is done over all chains and many independent runs. This measures the average deviation of a monomer from its position at $t = 0$.

The centre of mass correlation function $\langle R_{cm}^2(t) \rangle$ is defined as

$$\langle R_{cm}^2(t) \rangle = \langle [r_{cm}(t) - r_{cm}(0)]^2 \rangle \quad (5)$$

where

$$r_{cm}(t) = \frac{1}{L} \sum_{i=1}^L r_i(t). \quad (6)$$

Let $n_f(t)$ denote the number of moves accepted in the « forward » direction and $n_b(t)$ denote the number of moves accepted in the « backward » direction then

$$\langle s^2(t) \rangle = \langle [n_f(t) - n_b(t)]^2 \rangle \quad (7)$$

(the convention for the forwards and backwards direction is of course arbitrary). This function measures the mean square displacement of the polymer along its own arclength.

I also calculated the viscosity within the framework of the Doi-Edwards model. In this case the elastic modulus $G(t)$, is proportional to the amount of polymer left in the original tube and is straightforward to calculate numerically. Then using equation (3). I computed the viscosity by integration. It is questionable whether this procedure precisely gives the experimentally measured shear viscosity but it provides a well defined measure of the total relaxation time. A better measure of $G(t)$ would be obtained from studying the decay of birefringence of an initially anisotropic system. Though this better measure may be relevant to understanding the difference between viscosity and diffusion data, it is not discussed here due to difficulties in computation and interpretation. Preliminary numerical work indicates that a detailed understanding of $G(t)$ requires analysis of time scales longer than those considered in this paper. A detailed investigation of this problem will be the subject of a future paper.

Figures 3-9 display some results of the simulations for systems with different chain lengths and densities.

In figure 3, $\langle r^2(t) \rangle$ is plotted for different chain lengths. The systems illustrated all had identical densities of occupied sites maintained at

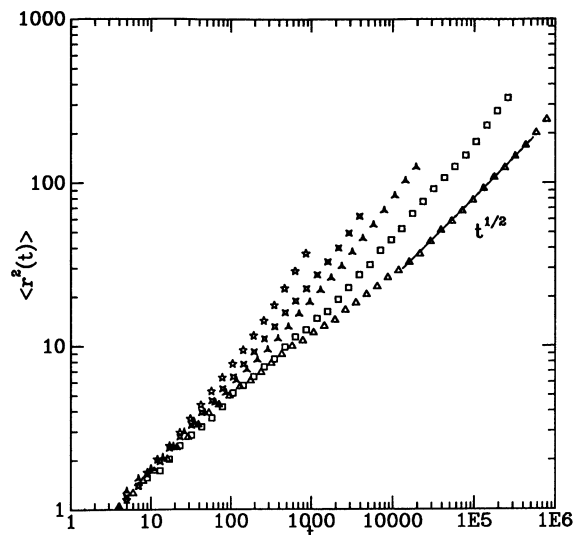


Fig. 3. — $\langle r^2(t) \rangle$ as a function of time for different chain lengths. These systems all have identical densities (62.22 %). The five sided stars are for runs with chain length $M = 10$, four sided : $M = 25$, three sided : $M = 50$, square : $M = 150$, and triangle : $M = 600$.

62.22 percent. The five sided star is for a system with chain length $M = 10$, four sided : $M = 25$, three sided : $M = 50$, square : $M = 150$, and triangle : $M = 600$. The box size was 15 for all runs except at 600 where it was 30. In the case of no excluded volume, and for long chains, there are two distinct slopes for $\langle r^2(t) \rangle$, on a log-log scale [6]. For times less than the relaxation time ($\propto M^2 \times \Delta t$), the slope of $\langle r^2(t) \rangle$ approaches but never goes below 1/2. For times longer than the relaxation time, the slope of $\langle r^2(t) \rangle$ approaches 1. In figure 3, which has the excluded volume constraint enforced however, the slope dips to below 1/2, indicating that motion is slowing down due to many chain interactions. Although this slowing down in the relaxation time is hard to detect for $M \leq 150$ (due to finite size effects), these effects are still present, as can be seen from data on viscosity (see below). For chains of length 600, three distinct regimes are present although the simulation was not run for long enough in time to probe the eventual diffusive regime $\langle r^2(t) \rangle \propto t$. A $t^{1/2}$ regime is marked by the solid line. Before this regime, the relaxation is much slower, though it is not clear what functional form would fit this slow relaxation best. Further numerical data presented in section 4, suggests that it is logarithmic.

Figures 4 and 5 illustrate $\langle R_{cm}^2(t) \rangle$ and $\langle s^2(t) \rangle$ for the same systems as in figure 3. Similar remarks apply to these curves regarding the slowing down of relaxation due to many chain interactions : for short times, the slopes of these two correlation functions are substantially smaller than in the no excluded volume case.

The viscosity computed from equation (3) was computed for the above systems. The results are displayed

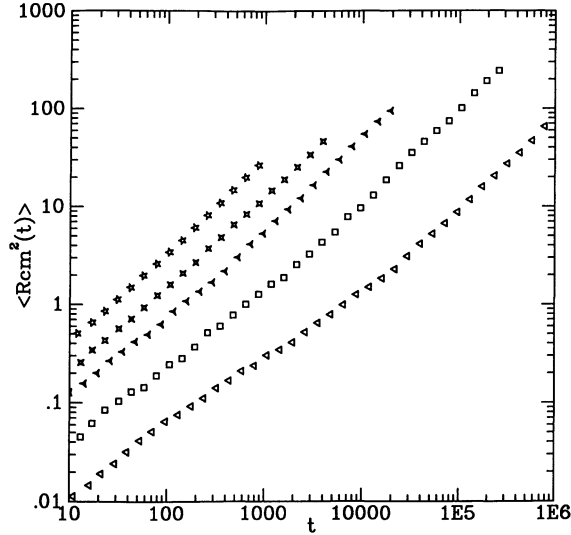


Fig. 4. — $\langle r_{cm}^2(t) \rangle$ as a function of time for different chain lengths. The systems and symbols are the same as in figure 3.

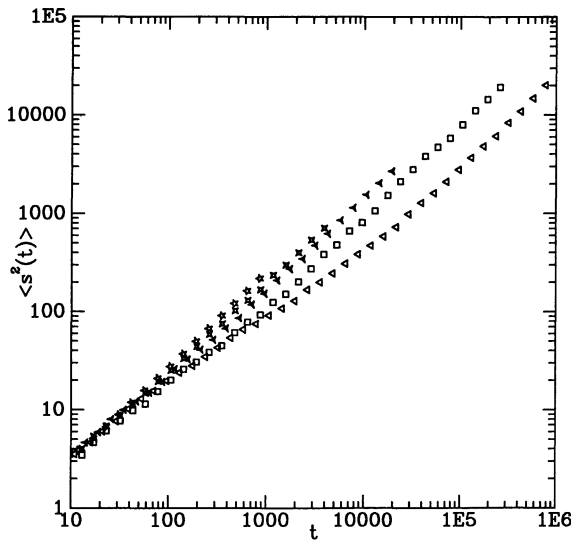


Fig. 5. — $\langle s^2(t) \rangle$ as a function of time for different chain lengths. The systems and symbols are the same as in figure 3.

for chain lengths going from 10 to 150 in figure 6. The lower solid line represents the results from reptation $\eta \propto M^2 \Delta t$, and the upper line gives

$$\eta \propto M^{2.4} \Delta t = M^{3.4}.$$

The diffusion coefficient (Fig. 7) was calculated by a least squares fit to a straight line done typically on the last ten data points displayed in figure 4. Again we see that the slope on this line is less than the no excluded volume case, represented by the solid straight line.

For comparison, the viscosity and the diffusion coefficient are displayed in figures 8 and 9 for simulations done at a density of 50 percent and a box size of 20. In both figures, higher molecular weight

chains are needed before deviations from the no excluded volume case become apparent.

The above results show that the addition of excluded volume interactions to the reptation model substantially slows down the motion of chains. This effect goes in the right direction in regard to experiments. A better understanding of the nature of this slowing down is needed before the relationship between these results and experiment can be ascertained. This is done in the next section.

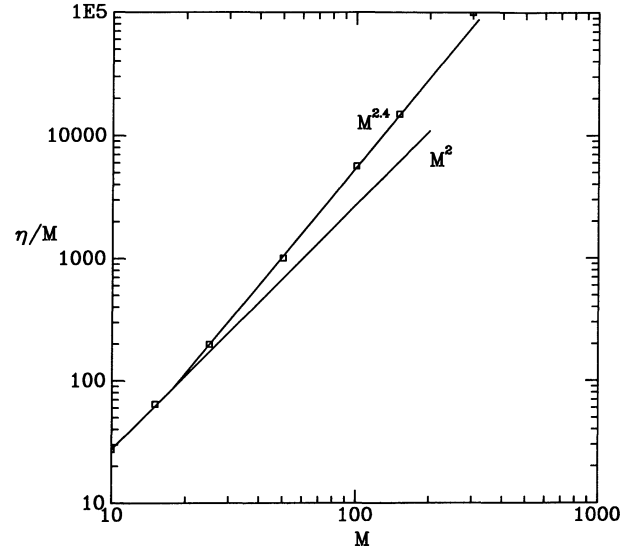


Fig. 6. — The viscosity η as function of chain length M for the same systems as in figure 3. The data points are squares, the solid line running through the data is $\eta/M \propto M^{2.4}$, and the line below it is $\eta/M \propto M^2$ which is the result obtained without the inclusion of excluded volume.

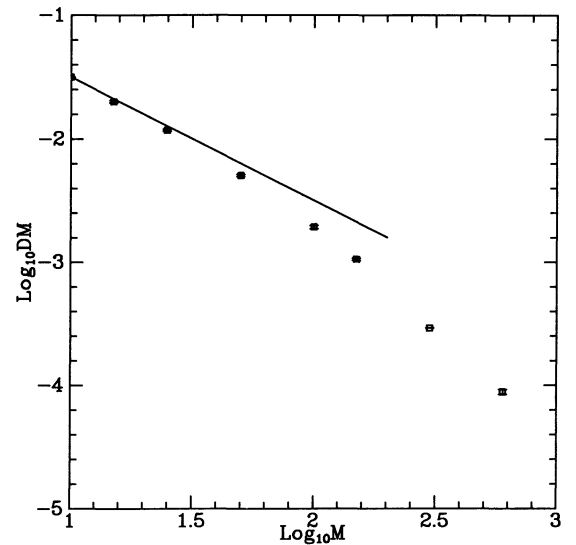


Fig. 7. — The diffusion coefficient D as function of chain length M for the same systems as in figure 3. The solid line is $DM \propto M^{-1}$ which is the result obtained without excluded volume.

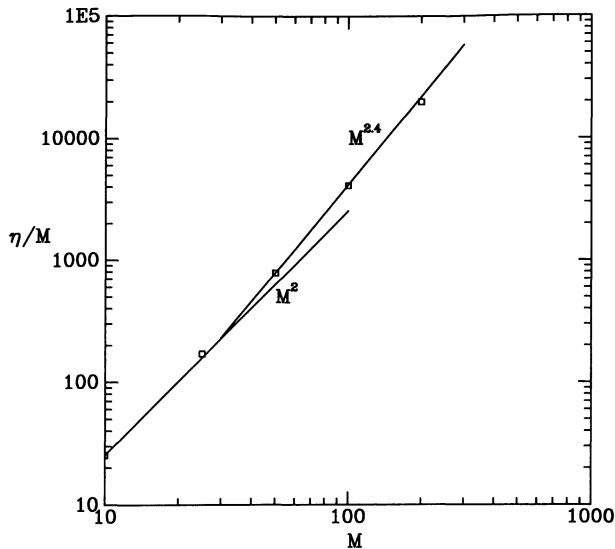


Fig. 8. — The viscosity as a function of chain length M for systems at a density of 50 %. The data points are squares, the solid line running through the data is $\eta/M \propto M^{2.4}$, and the line below it is $\eta/M \propto M^2$ which is the result obtained without the inclusion of excluded volume included.

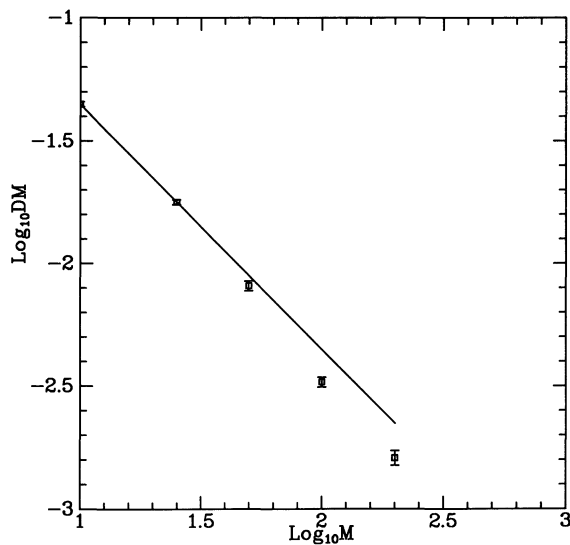


Fig. 9. — The diffusion coefficient as function of chain length M for systems at a density of 50 %. The solid line is $DM \propto M^{-1}$ which is the result obtained without excluded volume included.

4. Theory.

(i) Analysis of the simulation.

I will first develop a theory to explain the numerical results of section 3, and then consider its relation and extension to a real melt. Consider a long « black » polymer chain of unit step length in a melt of identical « white » chains initially in thermal equilibrium as shown in figure 10 (a). We now freeze the motion of the white chains but let the black one

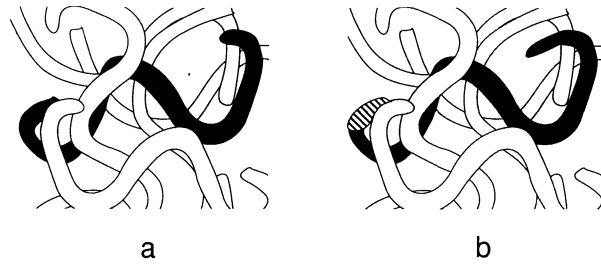


Fig. 10. — (a) A black chain in thermal equilibrium with a dense melt of white chains. (b) The black chain has reptated so that there is a density deficit close to one end (the striped region), and the other end sees a high density (marked in grey).

move according to reptation dynamics, as described above. Note that for long times, the freezing of the white chains leads to new and erroneous statistics for the black chain. However for short times, the black polymer should feel a frozen background, even if the other chains are moving, since changes in lattice occupation occur only at or near chain ends. Since the average distance between chain ends is proportional to $M^{1/3}$, then for times corresponding to chain end displacements of much less than $M^{1/3}$, the freezing of the white chains should be justified. Now in equilibrium, the total density of the melt is nearly constant. We see in figure 10 (b) that as the black polymer reptates it leaves behind a hole (striped region) and moves into a new region shown in grey with a higher than average density. Another way of viewing this is that the black chain sits in a « hole » which acts as an attractive potential, due to the absence of white polymer in this region. So we can think of the problem of a chain reptating in a melt as being equivalent (for short times) to a chain reptating in the presence of another *fixed* polymer (namely the original tube) with an attractive interaction between the tube and the polymer. We want to know the free energy of the polymer plus hole system as we vary the amount of overlap between the polymer and the hole. We expect that when the tube and the hole are nearly coincident, that the free energy will be lowest, but as the chain reptates away from the hole, the free energy should increase.

Note that the whole concept of a free energy of the hole plus polymer system is only meaningful if the polymer is localized around the hole for long enough that the polymer has almost equilibrated. This is similar in spirit to nucleation theory. We will see that, in analogy with nucleation, the height of the free energy barrier that the polymer has to overcome is very large (for large M).

We will analyse this system in mean field theory. This problem is similar to the adsorption of a polymer of length M next to a wall, since the fractal dimension of a random walk and a plane are both 2. Let us compute the entropy loss in confining a polymer to a width ΔR surrounding the tube (see Fig. 11). Within segments of radius ΔR , or lengths $\Delta M \sim \Delta R^{5/3}$, the polymer can take any configura-

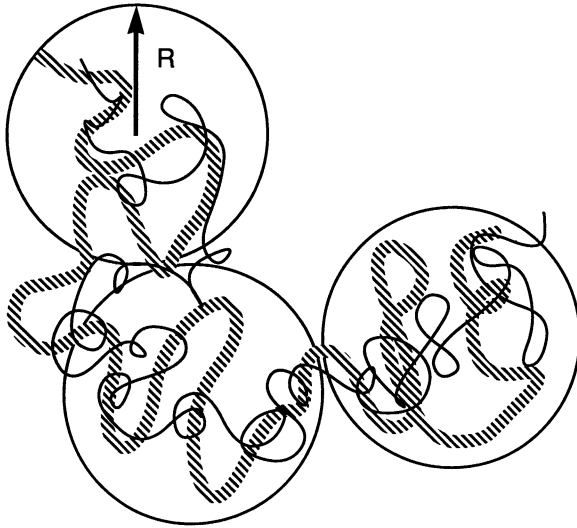


Fig. 11. — A chain (thin line) in equilibrium with a fixed hole (thick striped line). The chain is highly correlated with the hole at distances greater than ΔR , which is the radius of the circles illustrated.

tion. So only $M/\Delta M$ segments need be fixed in order to confine a polymer to the hole. This means the reduction in entropy is

$$S = \frac{M}{\Delta M} = \frac{M}{\Delta R^{5/3}} \quad (8)$$

(this is identical to (I.56) of de Gennes' [7]). Within ΔR , the number of intersections between the tube and the chain (of length ΔM) is proportional to the volume of this region times the density of tube times the density of chain, which gives the answer $\Delta M/\Delta R$. Balancing energy and entropy we find that the chain in equilibrium is confined to a small diameter around the hole given by

$$\Delta R \sim \delta^{-3/2} \quad (9)$$

where δ describes the amount of attraction between the polymer and the hole, and should be of order 1 in a concentrated system. The free energy of adsorption should be

$$F = \delta^{5/2} TM \quad (10a)$$

(see I.58 and I.59 of de Gennes [7]). Actually in the case discussed by de Gennes of polymer adsorption onto a plane, this kind of mean field analysis yields the incorrect dependence on δ , a more accurate analysis [8] of the δ dependence gives

$$F = \delta^{5/3} TM \quad (10b)$$

In the case of interest here, the dependence on δ may have a different exponent since we are interested instead in the adsorption of a polymer onto a random walk. In any case, there is a strong correlation between the tube and the hole. When the chain reptates a distance s out of its original tube it feels a reduction in free energy proportional to s . So the

chain should be localized about some equilibrium location with the probability of an excursion by an arclength s being proportional to $\exp(-\text{const.} \times s)$. As mentioned earlier, this analysis should only be valid for $s \ll M^{2/3}$, since the environment ceases to appear frozen for $s \geq M^{2/3}$ (or $r \geq M^{1/3}$). At these distances, relaxational processes can take place between chains that can alter the metastable configurations. As a polymer reptates it leaves a density deficit at one end and a density excess at the other. Another polymer a distance $M^{1/3}$ away can lower the free energy by either moving out of a high density region or into a low density one. There must be some complicated « shuffling » processes needed in order to rearrange chain ends after some new metastable configuration has been established. This analysis implies that it is necessary to surmount a free energy barrier of order $M^{2/3}$ which gives a relaxation time

$$t_{\text{rel}} \sim M^3 e^{\text{const.} \times M^{2/3} + O(M^{1/3})} \quad (11)$$

If we plot monomer displacement $r^2(t)$, we expect to see a logarithmic type relaxation for $t \ll M^2 \exp(M^{2/3})$ of the form

$$r^2(t) = \ln t \quad (12a)$$

and power law relaxation of the form

$$r^2(t) = M e^{M^{2/3}} t^{1/2} \quad (12b)$$

for $t \geq M^2 e^{M^{2/3}}$. This is indeed the kind of relaxation that was seen in numerical experiments (Fig. 3). To test these predictions more thoroughly, I ran a simulation where one chain could move but the rest were frozen, with $M = 300$, $B = 30$ and 62.22 percent of lattice sites filled. From the above argument, one would expect that the frozen system and a system of mobile chains should behave almost identically for times corresponding to motions of chain ends $\langle r^2(t) \rangle \ll M^{2/3}$ as in equation (12a). For times greater than this the mobile system should start moving much faster as in equation (12b), but the frozen system should continue to move slowly according to equation (12a) for much longer times. These predictions are confirmed by the numerical results displayed in figure 12, which shows that all three correlation functions measured are nearly identical up to 4 000 time steps which corresponds to $\langle r^2(t) \rangle \approx 15 (\approx M^{2/3}/3)$. However after this time, the frozen system moves much more slowly than the mobile system, with the slope of $\langle r^2(t) \rangle$ on the log log plot going down to about 0.15. Such slow growth of $r^2(t)$ is indeed reasonable confirmation of equation (12a), that is $r^2(t)$ appears to grow logarithmically.

(ii) Analysis for a real system.

Now I consider how the above results should be modified in the case of real melts with an entanglement length M_e . Here preservation of constant

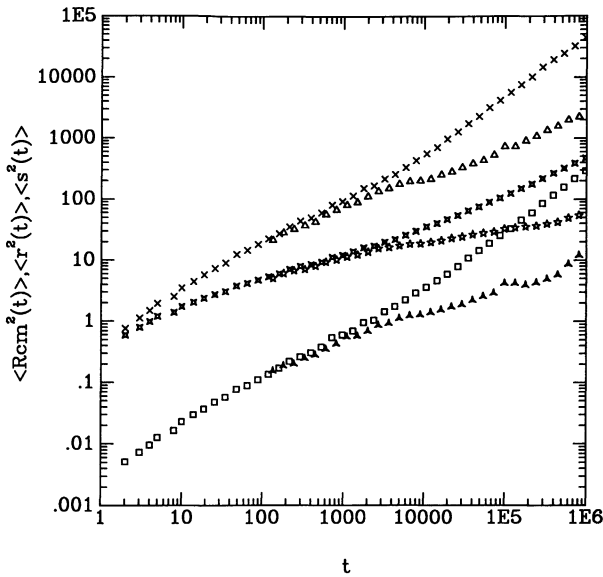


Fig. 12. — Correlation functions for a mobile set of chains and for one chain in a frozen environment. The density of the system is 62.22 %, and $M = 300$. In the mobile case, $\langle R_{cm}^2(t) \rangle$, $\langle r^2(t) \rangle$, and $\langle s^2(t) \rangle$ are illustrated by the squares, four sided stars, and crosses respectively. In the frozen case, $\langle R_{cm}^2(t) \rangle$, $\langle r^2(t) \rangle$, and $\langle s^2(t) \rangle$ are illustrated by the three sided stars, five sided stars, and triangles respectively.

density is not a problem. As the black polymer reptates it can push white chains out of the way. In the same way, a void created at the other end is easily filled in. What happens instead is that stress is generated in the regions that the polymer has entered, or vacated.

In other words, the main theoretical difference between the situation in the simulation, and a similar analysis of a real melt, is that in the computer model, changes in density are important, but in a real melt, it is local shear deformations that give rise to changes in the free energy. This is because a melt is virtually incompressible and density fluctuations relax very quickly, on a time scale of no relevance to the processes considered here. (In semi-dilute solution both local shear and compressional deformations contribute to changes in the free energy.) So what happens when a polymer end reptates into a new region, as shown in figure 10 ? We first consider the related question of what happens if one inflates a macroscopic balloon in a polymeric liquid [9]. On time scales less than the relaxation time, the melt behaves much like rubber. If we inflate a macroscopic balloon in a piece of rubber, the static pressure inside the balloon will increase due to the fact that the rubber in its immediate vicinity has been stretched. So one expects that in a polymeric liquid, the pressure in the balloon should decay in a time proportional to the relaxation time.

Now consider the question : what happens when the radius of the balloon becomes smaller than the

tube diameter ? I will argue in the following that the system behaves in the same way as it would with a large balloon, but with the modification that the stress field gets cut off at a radius of order the tube diameter D . That is, there is a stress field at distances larger than the tube diameter that can only relax through tube disengagement.

If we look at a point in a melt, a long distance r from an inflated balloon of radius R , then the radial displacement of that point after the balloon is inflated is $\delta r \sim R^3/r^2$ (assuming that the medium is incompressible). Clearly this formula is true even for an infinitesimally small balloon. So the change in free energy should be approximately

$$\Delta F \sim \int_D^\infty G \left(\frac{R^3}{r^3} \right)^2 r^2 dr \sim \frac{GR^6}{D^3} \quad (13)$$

where G is the plateau modulus ($\sim 1/M_e$). Note that the integral has been cut off at a distance of order the tube diameter. This is because stress induced by local deformations will relax almost instantaneously provided that we are looking at spatial frequencies with wavelengths smaller than the tube diameter D (since we are probing distances below the entanglement length). But at wavelengths larger than D , one would expect that there is a residual stress present due to orientational anisotropy which can only decay through tube disengagement.

This last point is in accord with the theory of Doi and Edwards (which only considers homogeneous deformations however). After an initial fast relaxation process, where monomer density adjusts so as to balance the tensile forces acting on primitive chain segments, the stress will have relaxed to a finite value, given by equation (4.8) of the second paper of Doi and Edwards (p. 1807). This resulting stress, due to anisotropy in the orientation of primitive chain segments, then relaxes through tube disengagement. For an inhomogeneous deformation varying on a length scale larger than the tube diameter, I see no additional mechanism for stress relaxation outside the two mentioned above.

An application of the above discussion is the calculation of the change in free energy induced by adding an entanglement length of chain to a melt. This amount of chain is equivalent to a balloon of volume $\sim R^3 \sim M_e$. Substituting this into equation (13) gives

$$\Delta F \sim 1/M_e^{1/2}. \quad (14)$$

To calculate the free energy increase induced by the black chain reptating an arclength S , one has to solve the following problem : what is the elastic energy when we inflate a thin cylindrical balloon in the shape of a random walk, and of total length S , up to some radius R ? To calculate the energy required to inflate a small balloon whose size is less than D , it is necessary to apply a small distance cutoff at D . How do we generalize this to an arbitrary strain field

$u(r)$? Normally the stress energy is

$$G \int |\nabla \mathbf{u}(\mathbf{r})|^2 d^3r. \quad (15)$$

But since the melt behaves like a liquid on length scales smaller than D , the most natural generalization of the above formula is

$$\Delta F = G \int \nabla \mathbf{u}(\mathbf{r}) \cdot \nabla \mathbf{u}(\mathbf{r}') g(\mathbf{r} - \mathbf{r}') d^3r d^3r' = G \int \sum_{i,j} |u_i(k)|^2 k_j^2 g(k) d^3k \quad (16)$$

where we could take $g(r)$ to be for example a Gaussian with width D . The last equality expresses the formula in terms of Cartesian coordinates and Fourier transformed variables. This has the effect of cutting off stress at spatial wavelengths of order D . So to find the elastic energy we minimize this equation subject to the constraint $\nabla \cdot \mathbf{u} = 0$. ΔF is a linear function of S , for large S . To see this, one can approximate the $\mathbf{u}$ field by linearly superposing the strain field of many infinitesimal spheres that are spaced uniformly along the path $\mathbf{r}(s)$, $0 < s < S$

$$\mathbf{u}(\mathbf{r}) \sim \int_0^S \frac{(\mathbf{r} - \mathbf{r}(s))}{|\mathbf{r} - \mathbf{r}(s)|^3} ds \quad (17)$$

or

$$u_i(\mathbf{k}) \sim \int \frac{k_i}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}(s)} ds \quad (18)$$

substituting this into equation (16) gives

$$\Delta F \sim G \int ds \int ds' \int \sum_{i,j} \frac{k_i^2 k_j^2}{k^4} g(k) \times \times e^{i\mathbf{k} \cdot (\mathbf{r}(s) - \mathbf{r}(s'))} d^3k \quad (19)$$

$$= \int_0^S ds \int_0^S ds' g(\mathbf{r}(s) - \mathbf{r}(s')). \quad (20)$$

Since $g(r)$ is short range, this is a linear function of S , for large S , but is $\propto S^2$ for $S < N_e$ since $g(r)$ has a width of order D .

Basically what the above results hinge on is the fact that if we inflate two balloons in an elastic medium, the energy required to do this is only very weakly dependent on the distance between the balloons. For a more general version of this fact see reference [10].

So the increase in free energy resulting from an excursion of the polymer by an arclength s should also result in an increase in free energy proportional to s . We also know the prefactor dependence on M_e if we assume the δ dependence of equation (10b) and also use equation (14). Since $g(r)$ has a range of order D , it is useful to think in terms of the primitive path of the polymer, which has a step length of D . Then $\delta = M_e^{-1/2}$. The distance between chain ends is $\propto M^{1/3}$, so the free energy barrier is the number of primitive path steps the polymer must reptate times the free energy per step which equals

$$M^{2/3} \frac{1}{M_e} \delta^{5/3} = \left((M/M_e)^{2/3} M_e^{2/3} \right) \frac{1}{M_e} M_e^{-5/6} = \left(M/M_e \right)^{2/3} M_e^{-7/6} \quad (21)$$

So the relaxation time in a melt should go as

$$t_{\text{rel}} \sim \frac{M^3}{M_e} e^{\text{const.}} \times (M/M_e)^{2/3} / M_e^{7/6} \quad (22)$$

The relaxation time in semidilute solution should also have the same exponential dependence on molecular weight, since one expects stress to be induced by a similar mechanism as in a melt.

5. Beyond the reptation model.

In this section I briefly look at an effect outside the reptation model that may alter the exponential dependence of the relaxation time from $t_{\text{rel}} \sim \exp(M^{2/3})$ to, for example $t_{\text{rel}} \sim \exp(M^{1/5})$.

There may be a very weak dependence of the tube diameter and the entanglement length on time, say $M_e \sim D^2 \sim \log t$. This may be due to polymer chains doubling up occasionally on themselves and moving perpendicular to the tube as shown in figure 13.

This kind of « weaving » motion is very slow and is closely related to the motion of star molecules [11]. In a polymer melt this effect may lead to a slow drift in the position of the tube due to the « weaving » of different polymers. So it may be possible that $D^2 \sim \log t$. This

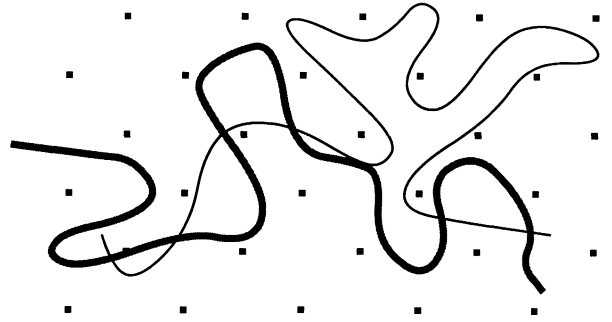


Fig. 13. — The thick line represents a chain in equilibrium with other chains, represented by the dots. The thin line represents the same chain at some later time after it has performed an unlikely motion that is completely disallowed in reptation theory.

kind of effect would be hard to detect experimentally but may be present. Equation (22) $t_{\text{rel}} \sim \exp(M^{2/3}/D^{1/3})$ can then be solved self consistently to eliminate D assuming $D^2 \sim \log t_{\text{rel}}$, giving $t_{\text{rel}} \sim \exp(M^{4/17})$. Of course this exponent depends on the precise variation of D with time. Therefore the exponential form of relaxation that I have predicted is sensitive to small departures from the reptation model. So unless the tube model is rigorously correct, an accurate calculation of the relaxation time is rather difficult.

6. Conclusions.

In this paper I have studied the dynamics of polymers in the framework of the reptation model but also including excluded volume interactions. At first sight, one might guess that in analogy with static properties of a melt, long range excluded volume interactions are screened out, however this turns out not to be the case. In particular other dynamical processes must come into play, in order to maintain screening in equilibrium. I have given a theoretical argument of how excluded volume interactions increase the relaxation time within the framework of the reptation model. This theory may provide an explanation for the experimental deviations of the viscosity from the predictions of the reptation

model. I have also performed a computer simulation which appears to agree quite well with experiment. The reader may ask how it is that experimental results show a power law behavior for the viscosity while the present theory predicts an exponential? If we plot $M^3 \exp(0.1 M^{2/3})$ versus M , then as can be seen (Fig. 14), over two decades it is quite close to $M^{3.4}$. Also this exponential prediction is only true in the limit of exceedingly long chains. The effects of fluctuations should be quite strong in the experimentally accessible regime. In fact the numerical work of section 3, suggests that this is the case as for chains of up to length 150, the relaxation time looks to be a power law.

The experimental determination of the diffusion constant in polymer melts is still the subject of much research with some conflicting results between different groups. Some groups [12] observe $D \propto M^{-2}$, while others [13] see a much lower exponent, roughly $D \propto M^{-2.8}$. Therefore at the present time it is difficult to compare diffusion data to the present theory which predicts that

$$D \propto M^{-2} \exp(-\text{const} \times M^{2/3} + O(M^{1/3})).$$

Furthermore to theoretically understand the relationship between viscosity and diffusion, the difficulties mentioned in the paragraph below equation (7) must be addressed.

Another explanation [14] for the viscosity data differing from the one in this paper, argues that the anomalous viscosity is a cross-over effect and that for very long chains $\eta \propto M^3$. Analysis of this idea appears to indicate that the cross-over effect is not strong enough to explain the experimental data over the entire range of molecular weight. However this explanation still cannot be dismissed and certainly deserves further investigation [15]. It might even be that for quite low molecular weights this effect dominates, but for higher molecular weights excluded volume effects become more important.

Acknowledgments.

I thank M. E. Cates, N. D. Goldenfeld, J. S. Langer and M. Marder for useful discussions. I especially wish to thank P. G. de Gennes for several useful correspondences on the material in this paper, which have greatly clarified my understanding of this subject. This research was supported by the National Science Foundation Grant No. PHY82-17853.

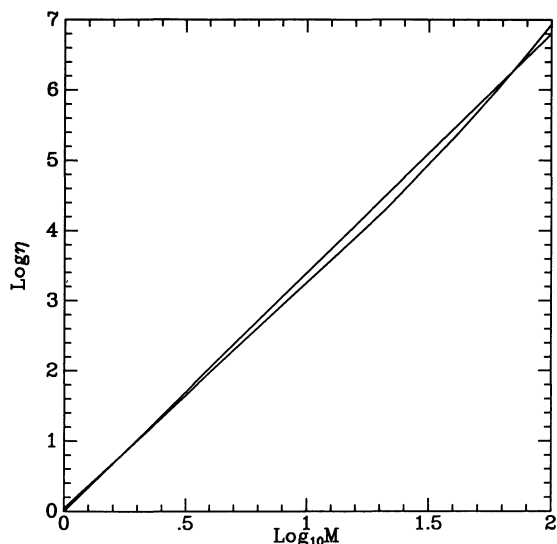


Fig. 14. — A comparison of the function $\eta = M^3 \exp(0.1 M^{2/3})$ (curved line) with $\eta = M^{3.4}$ (straight line).

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